On the Dialysis of Platinum-carbonyl Sol.

By Isamu SANO.

(Received April 19, 1940.)

It was described, in the preceding paper[1], that the platinum-carbonyl sol obtainable at ordinary temperature from a dilute aqueous solution of chloroplatinic acid by the action of carbon monoxide would, if left alone in the air for some time or submitted to dialysis, turn black from red colour to yield a platinum sol. This could be interpretted to be caused by the disappearance of carbon monoxide from colloidal particles owing to its volatilization towards as well as oxidation by the air during these processes. In fact, the red sol is so stable, if kept in touch with carbon monoxide, that it would be tinged, as it is, with red slightly inclining to purple for a long period. For instance, a platinum-carbonyl sol prepared from a 0.05% solution of the acid and hermetically sealed with the gas in a test-tube was scarcely charged with any appreciable change in colour for more than two years, though colloidal particles in the sol would come to display sedimentation in due course of time. The aspect of the red sol at several months after its preparation is illustrated in Fig. 1. Although the sol settled almost wholly about two years later, it could disperse with facility, if exposed to the action of supersonics, to be the same in appearance as ever

It may be presumed from these facts that, if dialyzed in the atmosphere of carbon monoxide, platinum-carbonyl sol will be set free, assuming red as it is, from hydrochloric acid liberated, in process of preparation, from chloroplatinic acid in consequence of its reduction by carbon monoxide. This was verified to be the actual case by the present experiment.

Experimental. The apparatus used is schematically shown in Fig. 2. Shortly after its formation, the red sol is transferred quickly and smoothly into the dialyzer, and immediately, subjected to dialysis, passing continually carbon monoxide through the sol as well as the dialyzate in turn. The dialysis was conducted with frequent changes of the dialyzate until freed from chlorine ions for a long space of time extending over fifteen days at room temperature, making use of a sheet of viscose in tubular form as the dialyzing membrane (M). Whenever the dialyzate was taken out through the cock (C) to be tested of chlorine ion, it was immediately supplied through the tube (T) from the reservoir (R) provided with a compression-valve (V). The conclusive test of chlorine ion was made directly with the sol in such a manner that a small portion of it was pipetted out from the dialyzer, converted by heating to a black sol of platinum, separated from suspending particles by dint of centrifuge, and now, submitted to the trial on chlorine ion.

(1) I. SANO, this Bulletin, **9** (1934), 320.

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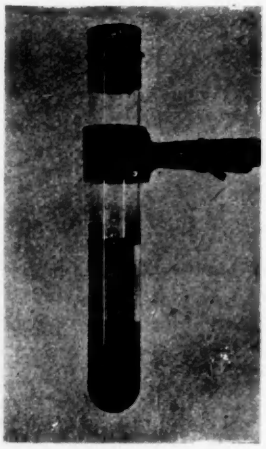

Fig. 1.

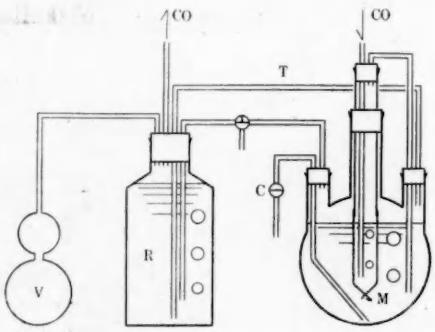

Fig. 2.

The experiments were made with the sols prepared at ordinary temperature in the same way as previously from 0.02 as well as 0.05% solutions of chloroplatinic acid. The sols obtained through the process of dialysis are the very same as they were before, not only in appearance but also in behaviour. For example, they assume a red colour which is slightly tinged with purple, decompose readily with the addition of bromine water or turn black, if left in the air or heated to some extent, to produce platinum sols. According to electrophoretic investigation, they are negatively-charged sols as ever.

It may be concluded from the results that the particles in the red sol, dialyzed or not, are composed only of platinum and carbon monoxide. The possibility of compounds containing chlorine as an essential constituent such as discussed in the preceding paper[1] would be not worth consideration. The formation of colloidal platinum surrounded by molecules of platinum-carbonyl has already[1] been substantially denied from various facts.

Summary.

The platinum-carbonyl sols of red colour prepared from 0.02 as well as 0.05% aqueous solutions of chloroplatinic acid were dialyzed in the atmosphere of carbon monoxide, as they would turn black to convert into platinum sols when treated in the air, until freed from chlorine ions.

The sols obtained through the process were just the same in appearance as well as in behaviour as they were formerly. This implies that the particles in the red sols, dialyzed or not, are fundamentally constituted from platinum and carbon monoxide or platinum-carbonyl.

The author wishes to express his sincere thanks to Prof. J. Sameshima for his kind guidance.

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The Action of Weak Alkalies upon Glucose. II.

By Ryuzaburo NODZU and Ryozo GOTO.

(Received April 26, 1940.)

The formation of acetol from glucose by the action of various alkaline reagents has been often reported. Concerning the mechanism of the formation, there have been two different views. Nef[1] postulated that the acetol is a reduction product of methylglyoxal which is formed from glucose through glyceric aldehyde. Pinkus[2], on the contrary, assumed it to be a primary decomposition product of the sugar. The former view has been supported by several investigators among whom Neuberg[3] put forward an opinion that methylglyoxal transforms disproportionately into acetol and pyruvic acid.

In the previous work[4], it was confirmed chemically and spectrographically that when a mixture of glucose and 1/25 mol solution of sodium carbonate (alone or with sodium sulphite) was distilled, acetol appeared along with diacetyl in the distillate. In the present work, aqueous solutions of glucose, glyceric aldehyde, methylglyoxal, and acetol were respectively distilled with sodium carbonate and the distillates analyzed (as semicarbazones), by methods similar to those described in the previous paper. In Table 1 the experimental results are tabulated.

Table 1.

No.	Sample		Na_2CO_3 $\frac{1}{25}$ mol sol. c c.	Na_2SO_3 g.	Distillate c c.	Iodine consuming substance as acetol g.	Semicarbazones g.	
	Name	g.					Diacetyl m.p. 278–80°	Acetol m.p. 196–7°
1	Glucose	5	250	15	1200	0.146	0.021	0.084
2	,,	5	250	0	1400	0.159	0.020	0.092
3	Methyl-glyoxal	3	250	15	1500	0.072	0.043	0
4	,,	3	250	0	1500	0.055	0.031	0
5	Glyceric-aldehyde	2	250	15	1500	0.075	0.014	0
6	,,	3	250	15	1000	0.117	0.023	Trace
7	,,	2	250	0	1500	0.068	0.011	0
8	,,	3	250	0	1000	0.093	0.020	0.010
9	Acetol	1	250	15	1500	0.382	0.001	0.411
10	,,	1	250	0	1500	0.343	0.002	0.400

(1) J. U. Nef, *Ann.*, **335** (1904), 247; **357** (1907) 214.
(2) G. Pinkus, *Ber.*, **31** (1898), 31.
(3) C. Neuberg, *Biochem. Z.*, **49** (1913), 502.
(4) R. Nodzu and R. Goto, this Bulletin, **11** (1936), 381.

As will be seen from the table, methylglyoxal gave not even a trace, glyceric aldehyde only a trace of acetol, and glucose an abundance of acetol. It was also found that the yield of acetol from glucose (Table 1. No. 1, 2.) was not increased by the addition of methylglyoxal in similar distillation experiments (Table 2.). Moreover, the origin of acetol from glyceric aldehyde (Table 1. No. 6, 8.) should rather be attributed to a hexose[5] which may be derived from the latter during the experiment in an alkaline medium.

Table 2.

No.	Sample		Na_2CO_3 $\frac{1}{25}$ mol sol c.c.	Na_2SO_3 g.	Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.	
	Name	g.					Diacetyl m.p. 278–80°	Acetol m.p. 196-7°
1	Glucose Methylglyoxal	5 1	250	15	1500	0.213	0.055	0.060
2	Glucose Methylglyoxal	5 1	250	0	1500	0.193	0.045	0.045

The acetol, therefore, is formed from glucose neither through glyceric aldehyde nor through methylglyoxal, showing that at least here, the postulations of Nef and others are untenable.

It is noteworthy that methylglyoxal distilled over from the weak alkaline solution as diacetyl, but not as itself, contradicting the assumption often made. It is very likely that under such conditions nearly all the methylglyoxal transforms easily into lactic acid and diacetyl (or acetoin).

Experimental Part. *Materials.* Methylglyoxal (b.p. 35°–38°/10 mm) was obtained by oxidation of acetone by means selenium dioxide[6]; and glyceric aldehyde (m.p. 130°) was prepared by way of acrolein acetal from glycerin following the Witzemann's method.[7] Acetol (b.p. 53°–54°/18 mm.) was synthesized from monobromoacetone by the method of Levene and Walti[8].

Distillation and Analysis. The distillation[9], the estimation of iodine consuming substances in the distillate, and the analysis of distillate were done in the same ways as described in the previous papers. The experimental results are tabulated in Tables 1 and 2. The distillation residue from methylglyoxal was evaporated to syrup under reduced pressure and the syrup was made strongly acidic by sulphuric acid. Then it was extracted with ether for about 30 hours, following[10] Evans' method.

(5) E. Schmitz, *Ber.*, **46** (1913), 2327; H. O. L. Fischer, *Helv. Chim. Acta*, **19** (1936), 519.

(6) H. L. Riley, J. F. Morley and N. A. C. Friend, *J. Chem. Soc.*, **1932**, 1875.

(7) E. J. Witzemann, *J. Am. Chem. Soc.*, **36** (1914), 1908.

(8) "Organic Syntheses." Vol. X, p. 1, (1930).

(9) During the distillation of methylglyoxal (alone or with glucose), 1/25 mol solution of Na_2CO_3 was supplied from time to time in order to keep a weak alkalinity of the distilling flask content.

(10) W. L. Evans and co-workers, *J. Am. Chem. Soc.*, **48** (1926), 2665.

From the ether extract, lactic acid was isolated in the form of its zinc salt (found: H_2O, 18.2; Zn 21.6; Calc. for $ZnC_6H_{10}O_6 + 3H_2O$:H_2O, 18.18; Zn 21.89%). Also, the acid was quantitatively titrated following Tanaka and Endo[11]. The analytical results are cited in Table 3.

Table 3.

No.	Methylglyoxal g.	Na_2CO_3 $\frac{1}{25}$ mol sol. c.c.	Na_2SO_3 g.	Distillate c.c.	Lactic acid in residue	
					g.	%
1	3	250	15	1500	0.654	21.8
2	3	250	0	1500	1.013	34.4

In conclusion, the expense of this work was defrayed by a grant (Sizenkagaku Kenkyu-hi.) from the Department of Education, to which the authors are deeply indebted.

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Acetylformoin. I. Its Preparation.

By Ryuzaburo NODZU and Sango KUNITIKA.

(Received April 30, 1940.)

Benzoylformoin[1] has long been known, but acetylformoin (a provisional formula $CH_3COCHOHCOCOCH_3$) has not previously been reported. It may be anticipated to be an interesting substance not only from the point of view of its structure, but also of sugar chemistry, being a possible dehydration product of the hexoses. In the present work, the preparation was effected by applying the principle of benzoin condensation to methylglyoxal.

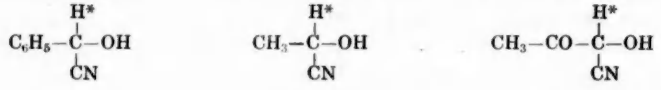
From the condensation product of methylglyoxal in the presence of potassium cyanide, a yellow crystalline substance was isolated by means

(11) S. Tanaka and M. Endo, *Biochem. Z.*, **210** (1929), 120.

(1) H. G. Söderbaum, *Ber.* **24** (1891), 1386, 3033.
P. H. Abenius and H. G. Söderbaum, *Ber.*, **25** (1892), 3470.
W. Abenius, *Ber.*, **27** (1894), 706.
P. Karrer and A. v. Segesser, *Helv. Chim. Acta*, **18** (1935), 273.
P. Karrer and C. Musande, *Helv. Chim. Acta*, **18** (1935), 1140.
P. Karrer and F. Litwant, *Helv. Chim. Acta*, **19** (1936), 829.
A. H. Blatt, *J. Am. Chem. Soc.*, **57** (1935), 1103; **58** (1936), 1894.

of vacuum distillation. On recrystallization from cold benzene, it formed pale yellow needles and melted at 81–82°. This substance has a molecular formula $C_6H_8O_4$ and may be either acyloin or aldol of methylglyoxal. Under similar experimental conditions, however, it was not formed by the action of hydroxyl ion alone—a proper catalyst for aldolization, indicating that the simultaneous presence of cyanide ion is essential for its formation. It was also observed that its hebaviour towards various oxidizing agents—Fehling's solution, ferric chloride and potassium permanganate, was quite similar to that of benzoylformoin. From these evidence, it may be concluded that it has a structure analogous to benzoylformoin and may properly be called acetylformoin.

By the action of aqueous alkali cyanide, aliphatic aldehydes, in general, give aldols, but no acyloin. The success in synthesizing acetylformoin seems at first sight to be somewhat surprising. In the previous articles,[2] however, we showed that it may be an essential condition for benzoin condensation that the hydrogen atom H* of a well accepted



(I) (II) (III)

intermediate—benzaldehyde cyanhydrine (I) is sufficiently acidic. The failure in the acyloin condensation of aliphatic aldehyde may, therefore, be attributed to a lack of acidity of the typical hydrogen in the intermediate, e.g., (II) being CH_3 a group far inferior to the C_6H_5 group in acidifying effect. On the other hand, the hydrogen atom of methylglyoxal cyanhydrine (III) would be sufficiently acidic, taking into consideration a powerful electromeric effect—an acidifying effect—of the CH_3-CO group. Methylglyoxal should therefore condense to acetylformoin, as it did in the actual case.

It should be noted that the aqueous solution of acetylformoin was fermented by Fleischmann's yeast, leaving the solution laevo-rotatory.

Experimental Part. *Methylglyoxal.* This was prepared from acetone by oxydation with selenium dioxide[3]. 850 c.c. of pure acetone was refluxed with 250 g. selenium dioxide for about 3 hours during which the liquid gradually became clear. After cooling the reaction liquid, the selenium powder deposited was filtered off and the filtrate distilled on a boiling water bath. The distillation residue was again distilled under reduced pressure and the fraction b.p. 39–41°/15 mm. was taken as methylglyoxal (yield 40 g.).

Acetylformoin. A methylglyoxal solution (40 g. in 200 c.c. water) and a potassium cyanide (3.1 g. mol ratio to methylglyoxal 0.083) solution were both cooled in ice water and then mixed. The mixture was made

(2) R. Nodzu and co-workers, *J. Chem. Soc. Japan*, **58** (1937), 313; **59** (1938), 1237.
(3) H. L. Riley, *J. Chem. Soc.*, **1932**, 1875.
J. Hahn and O. Schales, *Ber.*, **67** (1934), 1821.
T. Bersin, *Ber.*, **69** (1936), 560.

just alkaline (pH = 7.3) by addition of solid sodium bicarbonate, and kept for 30 minutes in ice water. After acidifying with syrupy phosphoric acid, it was evaporated under reduced pressure until inorganic salt began to crystallize out and then absolute alcohol (ca. 150 c.c.) was added. The deposited inorganic crystals were filtered off and the filtrate was evaporated to a syrup under reduced pressure. To the syrup, ether (ca. 350 c.c.) was added and the solution was filtered. The filtrate was dehydrated with anhydrous sodium sulphate and the ether driven away. The yellow syrupy residue was now subjected to a vacuum (5 mm.) distillation. At first an oily substance (ca. 4 g., b.p. 35–50°) distilled and as the thermometer rose from 60° to 70°, yellow crystals appeared in the condenser and on cold parts of the distilling flask. The crystals were gathered, and found to amount to about 4.5 g. They were recrystallized from cold benzene in fine pale yellow needles (m.p. 82.° Found: C, 50.1; H, 5.6; M, (in acetic acid) 142. Cal. for $CH_3COCHOHCOCOCH_3$: C, 50.0; H, 5.6%; M, 144.)

So far as studied under various conditions—of temperature, times and pH,—the reaction conditions described above were the best.

It was very auto-oxidizable, quickly darkened and liquefied in the course of 2 hours, when exposed to the air. It reduced Fehling's solution in the cold, and on addition of ferric chloride solution gave a greenish blue coloration which instantaneously faded when the solution was shaken.

Oxidation of acetylformoin. A solution of acetylformoin (0.12 g.) in 5% sulphuric acid (25 c.c.) was warmed on a boiling water bath, adding drop by drop 3% solution of potassium permanganate until no more decoloration of the oxidant took place. 8 c.c. of the permanganate solution was used. The reaction product was distilled, keeping its volume constant by the addition of water and the distillate was received in N/10 sodium hydroxide solution (25 c.c.). The distillation was continued until the distillate no longer reddened methylorange. On titration, it was found that it contained acid amounting to 0.0945 g. as acetic acid which corresponds to about 95% of the value calculated by the following equation

$$CH_3CO\cdot CHOH\cdot CO\cdot CO\cdot CH_3 \xrightarrow{+4O} 2\,CH_3COOH + 2\,CO_2$$

The amount of permanganate solution used was almost equal to what the theory requires (7.3 c.c.). From another experiment with 0.554 g. acetylformoin similar results were obtained, i.e., 34 c.c. (theoretically 33 c.c.) of the potassium permanganate solution was consumed and 0.425 g. acetic acid (92% of the theoretical) was formed. The distillates gave acetotoluidide (m.p. 147°).

Benzoylformoin (1 g.) was similarly oxidized (35 c.c. of 3% potassium permanganate solution) and benzoic acid (0.81 g.) was obtained with a yield of 96% of the theoretical value.

Action of potassium carbonate upon methylglyoxal. A solution of methylglyoxal (30–50 g. in 200 c.c. water) was made alkaline (pH 7.4–9.0) by potassium carbonate and kept for various intervals (0.5–15 hours) at 0–2°. After acidifying the reaction product with phosphoric acid, it was evaporated and extracted with ether. The ether extract was

evaporated and the residue was then distilled under reduced pressure without any sign of the appearance of acetylformoin. With ferric chloride the distillate (36–60°/3–5 mm.) did not show the characteristic greenish blue coloration of acetylformoin but rather a persistent red.

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Studies on Luminescent Materials. Part 2. On the Fluorescence Spectra of Zinc Sulphide-Copper Crystalphosphors at −185°, 20°, and 150°C*.

By Yasuo UEHARA.

(Received May 6, 1940.)

1. Introduction. In the previous paper[1], the author reported the theory of fluorescence, photoconductivity and the other properties of ZnS/Cu phosphors, based on the quantum mechanical theory of solid state. By the theory of the author, we can expect two fluorescence bands corresponding to the electronic transitions

$$^3D_2 \rightarrow {}^1S_0$$

$$^3D_3 \rightarrow {}^1S_0$$

of the Cu^+ ion in the activation centre of the ZnS/Cu phosphors.

In order to prove this expectation, the author carried out measurements of the fluorescence spectra of ZnS/Cu phosphors at −185°, 20°, and 150°C.

2. Experiments. (A) *Preparation of phosphors.* As raw materials, Kahlbaum's sample (guaranteed reagents for analytical purpose) were always used. These materials were purified by repeated recrystalizations or distillations. Zinc sulphide precipitate was prepared by a method similar to that of K. Mamm[2] and it was washed about fifty-times with distilled water. Then it was dried at 70°C. in an electric air bath with automatic regulator.

The resulting product is perfectly white fine powder. KCl was used as a flux and cupric sulphate water solution was added as an activator.

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* Read before the Annual Meeting of the Chem. Soc. Japan, April 5, 1939 and reported on the *J. Chem. Soc. Japan*, **60** (1939), 675.

(1) Y. Uehara: *Bull. Chem. Soc. Japan*, **14** (1939), 539; *J. Chem. Soc. Japan*, **60** (1939), 133.

(2) K. Kamm: *Ann. Physik*, **30** (1937), 333.

Finely ground mixtures whose compositions are shown in Table 1, were placed in a white alumina crucible which was placed in a larger crucible. They were heated in the sulphur vapour at 1100° ± 10°C. in an electric furnace with automatic regulator for 15 minutes and they were cooled rapidly.

Table 1. Composition of pure ZnS and ZnS/Cu phosphors.

No. of Sample	Activator	Flux
	Cu (gram atom)	KCl (mol)
ZnS—1	0	0
ZnS—2	0	1/10
ZnS—3	1×10^{-3}	1/10
ZnS—4	1×10^{-4}	1/10
ZnS—5	1×10^{-5}	1/10
ZnS—6	1×10^{-6}	1/10
ZnS—7	1×10^{-5}	0

(B) *Observation of fluorescence spectra.* In the measurements of fluorescence spectra, ZnS phosphor coated on a quartz tube, i.e. an inner tube in the Fig. 1, was irradiated by Hg 3650 Å (triplet) line and the emitted fluorescence light was introduced in about right angle in a spectrograph.

For the measurement at −185°C., the quartz tube covered with the phosphor was placed in a larger quartz tube and sealed with Apiazon W-wax at *D* in Fig. 1. After the space between the inner and the outer tube was evacuated, liquid air was poured into the inner tube.

For the experiments at 150°C., a furnace shown in Fig. 2 was used. In Fig. 2, *E* is ZnS phosphor placed in a quartz tube *C*, *F* and *D* are

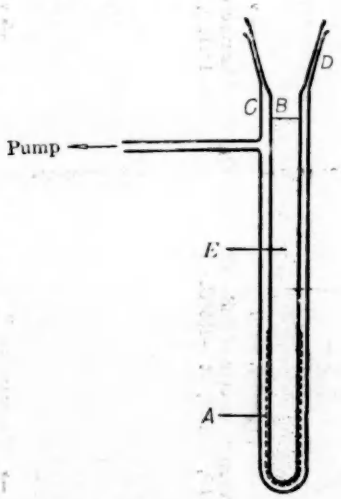

Fig. 1. Quartz tube for the measurements of the fluorescence spectra of ZnS phosphors. *A*: ZnS phosphor, *B*: inner quartz tube, *C*: outer quartz tube, *D*: Apiezon W-wax seal. *E*: liquid air.

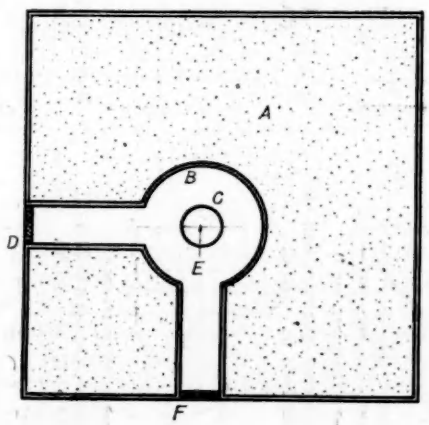

Fig. 2. Electric furnace for the measurements of Fluorescence spectra of ZnS phosphors at 150°C. *A*: electric furnace, *B*: aluminium metal wall, *C*: quartz tube, *E*: ZnS phosphor, *D*, *F*: quartz plate window.

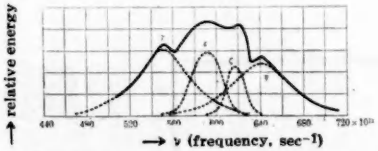

Fig. 3. Fluorescence spectra of ZnS—I (Cu=0, KCl=0) at −185°C.

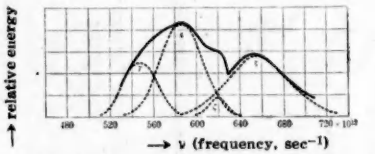

Fig. 4. Fluorescence spectra of ZnS—II (Cu=0, KCl=1/10) at −185°C.

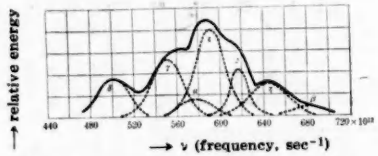

Fig. 5. Fluorescence spectra of ZnS—VII (Cu=1×10⁻⁵, KCl=0) at −185°C.

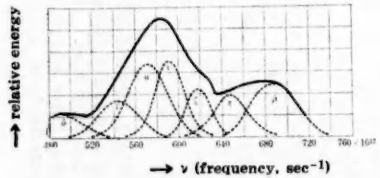

Fig. 6. Fluorescence spectra of ZnS—VI (Cu=1×10⁻⁶, KCl=1/10) at −185°C.

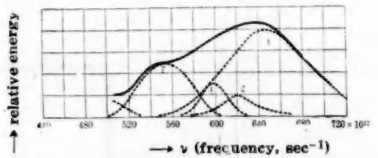

Fig. 10. Fluorescence spectra of ZnS—I (Cu=0, KCl=0) at 20°C.

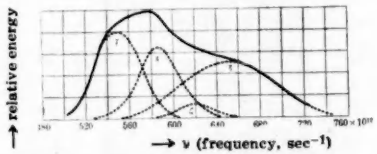

Fig. 11. Fluorescence spectra of ZnS—II (Cu=0, KCl=1/10) at 20°C.

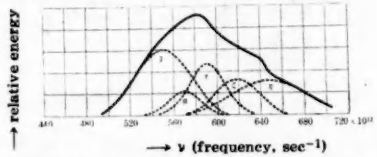

Fig. 12. Fluorescence spectra of ZnS—VII (Cu=1×10⁻⁵, KCl=0) at 20°C.

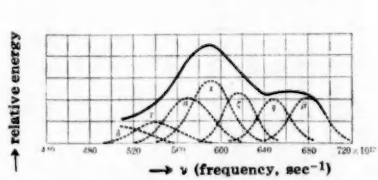

Fig. 13. Fluorescence spectra of ZnS—VI (Cu=1×10⁻⁶, KCl=1/10) at 20°C.

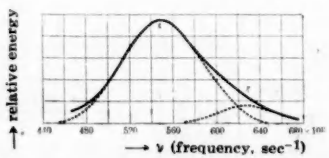

Fig. 17. Fluorescence spectra of ZnS—I (Cu=0, KCl=0) at 150°C.

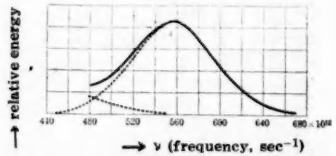

Fig. 18. Fluorescence spectra of ZnS—II (Cu=0, KCl=1/10) at 150°C.

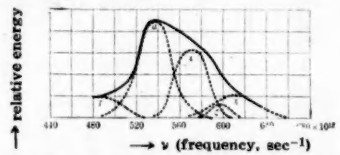

Fig. 19. Fluorescence spectra of ZnS—VII (Cu=1×10⁻⁵, KCl=0) at 150°C.

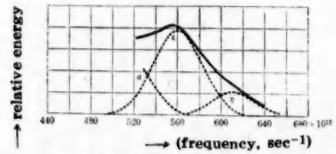

Fig. 20. Fluorescence spectra of ZnS—VI (Cu=1×10⁻⁶, KCl=1/10) at 150°C.

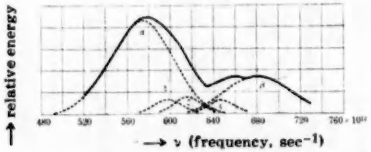

Fig. 7. Fluorescence spectra of ZnS—V ($Cu=1\times10^{-5}$, KCl=1/10) at −185°C.

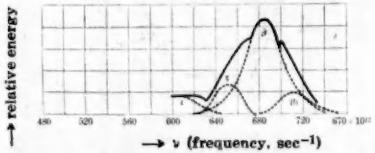

Fig. 8. Fluorescence spectra of ZnS—IV ($Cu=1\times10^{-4}$, KCl=1/10) at −185°C.

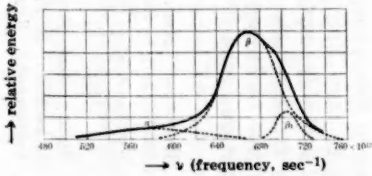

Fig. 9. Fluorescence spectra of ZnS—III ($Cu=1\times10^{-3}$, KCl=1/10) at −185°C.

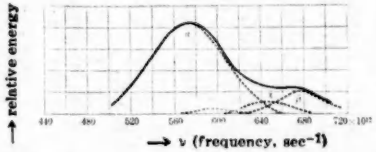

Fig. 14. Fluorescence spectra of ZnS—V ($Cu=1\times10^{-5}$, KCl=1/10) at 20°C.

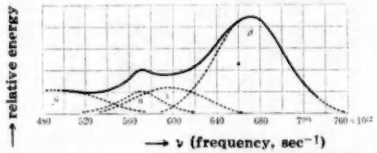

Fig. 15. Fluorescence spectra of ZnS—IV ($Cu=1\times10^{-4}$, KCl=1/10) at 20°C.

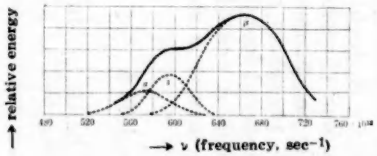

Fig. 16. Fluorescence spectra of ZnS—III ($Cu=1\times10^{-3}$, KCl=1/10) at 20°C.

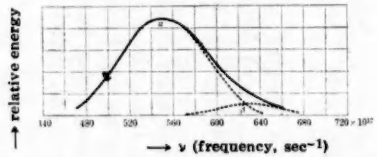

Fig. 21. Fluorescence spectra of ZnS—V ($Cu=1\times10^{-5}$, KCl=1/10) at 150°C.

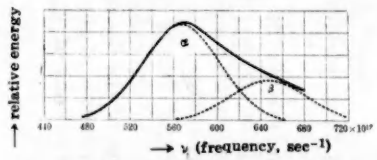

Fig. 22. Fluorescence spectra of ZnS—IV ($Cu=1\times10^{-4}$, KCl=1/10) at 150°C.

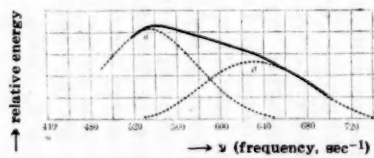

Fig. 23. Fluorescence spectra of ZnS—III ($Cu=1\times10^{-3}$, KCl=1/10) at 150°C.

quartz plate windows. The furnace in which the ZnS phosphor is contained, is kept at 150°C. by means of automatic regulator.

As the excitation light source, a high pressure mercury discharge tube in connection with a wood filter yielding practically only line of 3650 Å (triplet), was used.

Photographic spectrophotometry of the fluorescence spectra was made by means of Zeiss three glass prism spectrograph (focal length of camera lens: 27 cm.) in connection with a Zeiss fifth stepped filter and tungsten lamp as a standard light source.

The observed energy distribution curves of the fluorescence spectra were given in Fig. 3 ~ Fig. 23. In these figures thick lines show the observed energy distribution curves of the fluorescence spectra and broken lines show the energy distribution curves of the partial fluorescence bands ressolved by the similiar method to that of P. Borrissow[3], O. Schellenberg[4] and H. Nitka[5].

3. Theoretical Interpretation of the Experimental Results. (A) *Fluorescence of pure* ZnS *phosphors.* Fluorescence of pure ZnS phosphors containing no activator was observed first by A. Schleede[6] and later by N. Riehl[7] and by S. Rothschild[8]. Rothschild[8] reported that pure ZnS phosphors which contain NaCl as a flux but no activator, show only one fluorescence band with a maximum at 466 mμ. In the pure ZnS phosphors containing no flux and no activator, however, the author observed four (partial fluorescence bands with maxima at 4670 Å, 4870 Å, 5085 Å and 5455 Å at -185°C., as shown in Fig. 3. The author proposes to give a following nomenclature for these four fluorescence bands,

$$\eta = 4670 \text{ Å} \qquad \zeta = 4870 \text{ Å} \qquad \varepsilon = 5085 \text{ Å} \quad \text{and} \quad \gamma = 5455 \text{ Å}.$$

In these bands, η=4670 Å band will probably correspond to the band 466 mμ observed by Rothschild.

Tomaschek[9] observed four bands in the ZnS phosphor activated by by Cu, $\alpha = 520$ mμ, $\beta = 437$ mμ, $\gamma = 570$ mμ, and $\delta = 600$ mμ. Rothschild[8] assumed that $\gamma = 570$ mμ band observed by Tomaschek will not be due to Cu activator but to Mn activator which might be involved as impurities in this phosphor. The author, however, observed $\gamma = 5455$ Å band in the pure ZnS phosphor containing no impurities. $\gamma = 5455$ Å band will probably correspond to $\gamma = 570$ mμ band observed by Tomaschek. Then we can conclude that γ band is not due to Cu activator or Mn activator but to Zn atom activator diffused in this phosphor, as shown in our previous paper.[1]

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(3) P. Borrissow: *Ann. Physik.* **42** (1913), 1321.
(4) O. Schellenberg: *Ann. Physik.* **13** (1932), 249.
(5) H. Nitka: *Ann. Physik.* **16** (1933), 720.
(6) A. Schleede and H. Rupp: Die Leuchtmassen und ihre Verwendung, Borntraeger (1937), 153.
(7) N. Riehl: *Ann. Physik.* **29** (1937), 637.
(8) S. Rothschild: *Z. Physik.* **108** (1937), 24.
(9) R. Tomaschek: *Ann. Physik.* **65** (1931), 212.

It is pointed out by Seitz[10] that the presence of excess of Zn atom is responsible for the fluorescence of pure ZnS phosphors. But Seitz's mechanism of fluorescence of pure ZnS phosphors is different from that of the author, as shown already in the previous paper.[1]

The author has pointed out in the previous paper[1] that the resonance radiation (in its wide meaning) in the activation centre is responsible for the fluorescence of pure ZnS phosphors as well as ZnS phosphors activated by Cu. Fig. 24 shows schematically the energy levels of pure ZnS phosphors and of ZnS phosphors activated by Cu. (cf. Uehara.[1])

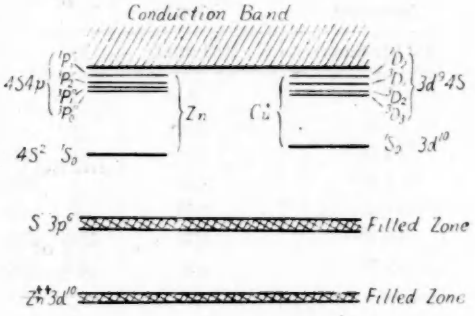

Fig. 24. Energy level diagram of the pure ZnS and ZnS/Cu phosphor.

The energy levels of normal Zn atom lies in the forbidden region between conduction band and S^{--} $3p^6$ band. The energy levels of excited Zn atom lies immediately below the conduction band or on the position overlapping partially each other. Fig. 25 show the potential curve of Zn atom in the activation centre schematically. *A* represents an equilibrium position of the normal Zn atom in the activation centre. After an electron in this position has absorbed light quanta, it makes a transition to one of the excited states of Zn atom. Then it moves into a new equilibrium position of the excited states. The transition of the electron from the excited states to the ground state gives rise to the four fluorescence bands in the pure ZnS phosphors. But it is very difficult to predict which of these transitions corresponds to each band of these four fluorescence bands. Therefore, we assume that the four fluorescence bands observed by the author may be correlated with following electronic transitions, (cf. Fig. 25),

$$^1P_1 \rightarrow {}^1S_0\ (a \rightarrow i) = 4670\ \text{Å} = \eta$$

$$^3P_2 \rightarrow {}^1S_0\ (b \rightarrow h) = 4870\ \text{Å} = \zeta$$

$$^3P_1 \rightarrow {}^1S_0\ (c \rightarrow g) = 5085\ \text{Å} = \varepsilon$$

$$^3P_0 \rightarrow {}^1S_0\ (d \rightarrow f) = 5455\ \text{Å} = \gamma\ .$$

The reason for this assumption will be given to some extent in the following discussion about the fluorescence of ZnS/Cu phosphors.

By using this mechanism of the fluorescence of pure ZnS phosphors, the author could calculate theoretically the temperature dependence of the photoconductivity and of the intensity of the fluorescence of pure ZnS phosphors as well as ZnS phosphors activated by Cu, as we shall see in the following paper.

(B) *Fluorescence of* ZnS/Cu *phosphors.*

As we see in Table 2 ~ Table 4, there exists three fluorescence bands α, β and β_1 due to activator in the ZnS phosphors activated by Cu, Fig. 26

(10) F. Seitz: *J. Chem. Phys.* **6** (1938), 150.

Table 2. Fluorescence band of pure ZnS and ZnS/Cu phosphors at −185°C. (Wave length unit Å)

Activator	Flux	Fluorescence bands							
Cu (gr atom)	KCl (mol)	β_1	β	η	ζ	ε	α	γ	δ
0	0	—	—	4670	4870	5085	—	5445	—
0	1/10	—	—	4585	4840	5120	—	5475	—
1×10^{-5}	0	—	4410	4660	4870	5085	5300	5455	6120
1×10^{-6}	1/10	—	4380	4645	4870	5085	5270	5535	6120
1×10^{-5}	1/10	—	4410	4645	4885	5050	5225	—	—
1×10^{-4}	1/10	4225	4375	4615	—	—	—	—	—
1×10^{-3}	1/10	4265	4480	—	—	—	—	—	—
	Mean	4245	4410	4635	4865	5085	5260	5480	6120

Table 3. Fluorescence bands of pure ZnS and ZnS/Cu phosphors at 20°C. (Wave length unit Å)

Activator	Flux	Fluorescence bands						
Cu (gr atom)	KCl (mol)	β	η	ζ	ε	α	γ	δ
0	0	—	4645	4855	5035	—	5455	—
0	1/10	—	4600	4840	5120	—	5475	—
1×10^{-5}	0	—	4645	4855	5085	5270	5455	—
1×10^{-6}	1/10	4410	4645	4870	5085	5265	5555	—
1×10^{-5}	1/10	4445	4645	—	5050	5245	—	—
1×10^{-4}	1/10	4480	—	—	5040	5265	—	6120
1×10^{-3}	1/10	4520	—	—	5050	5265	—	—
	Mean	4465	4635	4855	5065	5260	5485	6120

Table 4. Fluorescence bands of pure ZnS and ZnS/Cu phosphors at +150°C. (Wave length unit Å)

Activator	Flux	Fluorescence bands				
Cu (gr atom)	KCl (mol)	β	η	ζ	ε	α
0	0	—	4840	—	5475	—
0	1/10	—	—	—	5415	—
1×10^{-5}	0	—	4920	5035	5265	5595
1×10^{-6}	1/10	—	4920	—	5355	—
1×10^{-5}	1/10	4760	—	—	—	5455
1×10^{-4}	1/10	4645	—	—	—	5300
1×10^{-3}	1/10	4760	—	—	—	5595
	Mean	4755	4895	5035	5375	5485

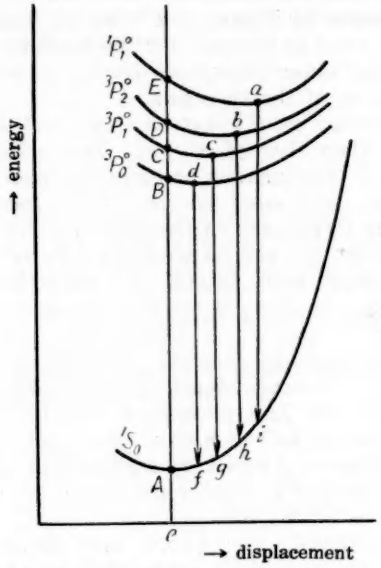

Fig. 25. Potential curve of Zn atom in the activation centre of the pure ZnS phosphor.

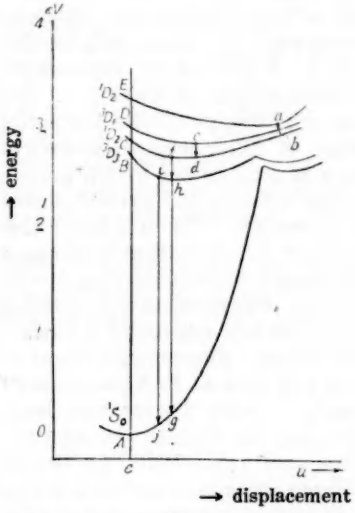

Fig. 26. Potential curve of Cu^+ ion in the activation centre of the ZnS/Cu phosphor.

shows the potential curve of Cu^+ ion in the activation centre, which has been already given by the author.[1] When an electron in the equilibrium position of one of the excited states of Cu^+ ion in the activation centre makes a transition to the ground state of Cu^+ ion, fluorescence will be observed. For example, the electronic transitions $f \rightarrow g$ or $i \rightarrow j$ give rise to fluorescence. On the other hand, the transition $f \rightarrow h$ will occur with radiation of elastic vibration wave and this transition will be more probable compared with the transition $f \rightarrow g$, when the coupling between the electron and lattice vibrations is strong.

Therefore, the transition $f \rightarrow g$ will become more probable compared with the transition $i \rightarrow j$, when the amplitude of the elastic vibrations in the activation centre becomes small. In other words, the lower the temperature is, the stronger the fluorescence band corresponding to the transition $f \rightarrow g$ becomes. As we see in Fig. 4 ~ Fig. 23, when the temperature decreases the blue β (and β_1) band becomes stronger compared with the green α band. Therefore, we can say that α and β band may be correlated with the following transitions.

$$^3D_2 \rightarrow {}^1S_0 \ (f \rightarrow g) = \beta$$

$$^3D_3 \rightarrow {}^1S_0 \ (i \rightarrow j) = \alpha$$

By the same reason, the transition $^3D_1 \rightarrow {}^1S_0$ may be responsible for the band β_1, which has the shortest wave length. $\delta = 6120$ Å band

observed by the author in some of the ZnS/Cu phosphors will probably correspond to the $\delta = 600$ mμ band observed by Tomaschek. But nothing can be predict about the origin of the δ band at present, for the measurements of the fluorescence spectra of the other phosphors have not yet been carried out thoroughly in this region of the spectrum.

(C) *Effect of the amount of activator on the fluorescence spectra.* The ionic radius of Cu^+ ion is smaller than that of S^{--} ion. Hence the larger the amount of the Cu activator is, the smaller becomes the overlapping of their eigenfunctions in the activation centre. Therefore, when a large amount of Cu^+ activator is introduced in the phosphor, the coupling between the excited states of Cu^+ ion and lattice vibrations will become weaker. Then β-band should occur more intensively, when the amount of Cu activator becomes larger. In fact, it is the case in our observations, as seen in Fig. 4 ~ Fig. 23.

(D) *Effect of the flux on the fluorescence spectra.* It could not be observed any appreciable variations of the wave length of the maxima of the partial fluorescence band between the ZnS phosphors containing no flux and that of ZnS phosphors containing KCl as a flux. But relative intensity of each fluorescence band varies very much by adding KCl as a flux. As the results, the energy distribution curves of the fluorescence spectra vary remarkably by the influence of the flux.

From these results, we can consider that K^+ (or Cl^-) ion may diffuse into the crystal lattice and it changes the transition probability of the electron from the excited states to the ground state in the activation centre.

(E) *Temperature effect on the fluorescence spectra.* It has been already pointed out by the author that the fluorescence band of ZnS phosphors should show a wide breadth by the molecular vibrations coupled with the elastic vibrations of the lattice.[1] Therefore, the breadth of the bands should become larger when the temperature is raised, which was actually the case in the observations by the author. Further it could be confirmed experimentally that the wave length of the maxima of the partial fluorescence bands make a shift from blue to red with increasing temperature above the room temperature.

Summary.

(1) Energy distribution curves of the fluorescence spectra of pure ZnS and ZnS/Cu phosphors were measured at –185°, 20°, and 150°C.

(2) Four fluorescence bands were observed in the pure ZnS phosphors containing no activator and no flux. It was pointed out that these four fluorescence bands may be correlated with the transitions

$$^1P_1 \rightarrow {}^1S_0 = 4670\ \text{Å} = \eta$$

$$^3P_2 \rightarrow {}^1S_0 = 4870\ \text{Å} = \zeta$$

$$^3P_1 \rightarrow {}^1S_0 = 5085\ \text{Å} = \varepsilon$$

$$^3P_0 \rightarrow {}^1S_0 = 5455\ \text{Å} = \gamma$$

of the electron of the Zn atom in the activation centre.

(3) In the ZnS phosphors activated by Cu, three bands α, β and β_1 were observed. These three fluorescence bands may be correlated with the transitions

$$^3D_3 \rightarrow {}^1S_0 = 5260\ \text{Å} = \alpha$$

$$^3D_2 \rightarrow {}^1S_0 = 4410\ \text{Å} = \beta$$

$$^3D_1 \rightarrow {}^1S_0 = 4245\ \text{Å} = \beta_1$$

of the electron of the Cu^+ ion in the activation centre.

(4) The effect of the temperature and of the amount of the activator, and flux on the fluorescence spectra were discussed.

The author wishes to express his sincere thanks to Mr. B. Imamura, Vice-Director of this institute, for his generous help and to Prof. S. Mizushima of Tokyo Imperial University for his kind advice and encouragement.

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Catalytic Activity of Phthalocyanines in the Autoxidation of Linseed Oil and Methyl Linoleate.

By **Bunichi TAMAMUSHI** and **Shizuo TOHMATSU.**

(Received May 13, 1940.)

Phthalocyanine and its related compounds have been in these ten years extensively studied by Linstead and his co-workers.[1] Among many remarkable results obtained concerning these compounds, their catalytic properties are of special interest. Polanyi and his co-workers[2] have found that metal-free phthalocyanine as well as copper phthalocyanine are capable to activate molecular hydrogen and to catalyse the conversion of para-hydrogen into normal hydrogen. Cook[3] has recently demonstrated that iron phthalocyanine and its related compounds have similar catalytic properties as haemin and other iron-containing compounds of porphyrin group, which are important from a biochemical point of view. They possess namely catalase and oxidase properties and are capable of catalysing the decomposition of hydrogen peroxide, the

(1) R. P. Linstead, Phthalocyanine und verwandte Verbindungen, ein zusammenfassend. Vortrag., *Ber.* **72** (1939), A, 93.

(2) M. Polanyi, M. Calvin and E. G. Cockbain, *Trans. Faraday Soc.* **32** (1936), 1436, 1443.

(3) A. H. Cook, *J. Chem. Soc.* **1938**, 1761, 1768, 1774, 1845.

oxidations of hydrogen iodide, benzaldehyde and a number of olefinic compounds and the chemiluminescent reaction of luminol.

According to our own observations, a weak luminescence came out, when 0.05%-luminol solution in 5%-aqueous NaOH was treated with 3%-hydrogen peroxide in the presence of a small amount of chloriron phthalocyanine, while with copper- or magnesium phathalocyanine the reaction occurred so feebly that the emitted light was only just discernible. The catalase activities of these compounds were examined in aqueous solution of hydrogen peroxide in which a small amount of catalyst was suspended, the course of decomposition being normally followed by titration with potassium permanganate. The first order velocity constant thus determined at 20°C. are approximately 0.01 min.$^{-1}$ for chloriron phthalocyanine, 0.001 min.$^{-1}$ for magesium- and copper phthalocyanine, whereas the velocity constant of haemin is about 0.05 min.$^{-1}$ The catalase activity of chloriron phthalocyanine is therefore about 1/5 of that of haemin, which is in accordance with the fact that chloriron phthalocyanine is highly surpassed by haemin in the catalytic influence upon the luminescent oxidation of luminol.

Now, some of the compounds of phthalocyanine are used as colours. They are valuable because of their beauty of appearance, strong colouring power, unusual stability against light, heat, alkali, and acid and insolubility in ordinary solvents. Granted that they have more or less the oxidase activity, it is a matter of interest to examine whether they themselves act as driers, when they are used as colours in paints. Mr. Akiyama, who kindly afforded us metallic pathalocyanines[4] and other materials used in the present experiment, made some preliminary observations on this subject. Among the metallic phthalocyanines, chloriron phthalocyanine was found to be effective as a drier, though its efficiency was not so great as that of Co-Pb-naphthenate ("Soligen") of I. G., a well known drier.

We first determined the rate of drying of linseed oil at 50°C. in air, once with Co-Pb-naphthenate and then with metallic phthalocyanines, the oil being well mixed with a small quantity (0.05 g. per 1 c.c. oil) of catalyst. The linseed oil with Co-Pb-naphthenate dried in about 3 hours, while with chloriron phthalocyanine in about 7 hours and with copper or magnesium phthalocyanine in about 25 hours.

We then made some experiments concerning the catalytic action of metallic phthalocyanines as compared with that of Co-Pb-naphthenate of I. G. towards the autoxidation of methyl linoleate and linseed oil. Methyl linoleate has been prepared from cotton seed oil as follows:[5] 1 kg. cotton-seed oil is saponified and fatty acids thereby obtained are dissolved in 1500 c.c. ligroin, into which bromine is added under cooling until a red colour comes to stay. The bromination product is recrystallized from ligroin. The bromide together with methyl alcohol and zinc granules is then heated till the mixture boils, and into it is added methyl alcoholic

(4) The method of preparation of metallic phthalocyanines adopted by Mr. Akiyama is principally the same as that of Linstead and his co-workers. Compare *J. Chem. Soc.*, **1934**, 1017-1031.

(5) Beilstein, Organische Chemie, Bd. II, 496.

hydrochloric acid: the mixture is again boiled for an hour. On cooling, the methyl ester of linoleic acid separates itself, which is extracted with petroleum ether and washed with water several times and dried by means of sodium sulphate: petroleum ether is then expelled by evaporation. The pure product is obtained by distillation in vacuo.

Linseed oil as well as methyl linoleate were dissolved in carbon tetrachloride with catalyst (0.015 g. catalyst in 50 c.c. solution) in a reaction vessel with upright cooling condenser, into this mixture air was gently passed through for 20–24 hours, during which time the reaction vessel was maintained at a constant temperature of 20°C. From time to time, a small portion of the solution was pipetted out, of which the iodine number was determined according to the method of Wijs and thus we compared the rate of autoxidation.

The results are given in the following tables, one for methyl linoleate and another for linseed oil, where chloriron phthalocyanine and Co-Pb-naphthenate are compared as to their catalytic activity.

Table 1. Autoxidation of Methyl Linoleate.

With chloriron phthalocyanine as catalyat		With Co-Pb-naphthenate as catalyat	
Time (hours)	Iodine number	Time (hours)	Iodine number
0	174	0	174
3	130	3	104
10	92	10	85
20	75	20	70

Table 2. Autoxidaton of Linseed Oil.

With chloriron phthalocyanine as catalyst		With Co-Pb-naphthenate as catalyst	
Time (hours)	Iodine number	Time (hours)	Iodine number
0	175	0	175
3	140	2.5	136
10	91	10	90
24	62	24	61

The accuracy of the determination of iodine number was not the same in all cases and allowance should be made for errors due to the variation of concentration of the reacting mixture in the course of the reaction time. The general features of the matter are nevertheless evident. Chloriron phthalocyanine has, as is shown above, really a marked catalytic activity towards the autoxidation of methyl linoleate as well as of linseed oil; its activity is almost as powerful as that of Co-Pb-naphthenate, although the latter always excels the former.

Out of other metallic phthalocyanines copper phthalocyanine was chosen and examined, whose activity was, however, found to be much weaker than that of chloriron phthalocyanine, the iodine number of methyl linoleate decreasing from 174 to 110 in 20 hours while that of linseed oil from 175 to 120 in the same time.

Summary.

The catalytic action of metallic phthalocyanines towards the autoxidation of linseed oil and methyl linoleate is demonstrated. Chloriron phthalocyanine is remarkably effective as catalyst, whereas copper- and magnesium phthalocyanine are slightly effective.

We deeply acknowledge our indebtedness to Mr. H. Akiyama of Nippon Oil and Fat Co. for his kind supply of materials as well as his valuable advices. We also thank the Nippon Gakuzyutu Sinkokai for a grant.

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Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. IX. Die Herstellungsmethode und die katalytische Wirksamkeit des Katalysators: die mischkatalytische Wirkung der Verunreinigungen.[1]

Von **Noriyoshi MORITA.**

(Eingegangen am 15. Mai 1940.)

Inhaltsübersicht. Der mögliche Einfluss der Verunreinigungen, die bei der Herstellung des Katalysators eintreten können, auf die katalytische Wirksamkeit des letzteren für die Austauschreaktion zwischen Wasserdampf und Sauerstoffgas wird durch ein besonderes Experiment untersucht, das unter Benutzung der auf verschiedene Weise hergestellten Arten der Kupferoxyde durchgeführt wurde. Dabei wird festgestellt:

(a) Die vier Arten der Kupferoxyde, die resp. auf verschiedene Weise hergestellt wurden und voneinander ziemlich stark verschiedene äusserliche Beschaffenheit besitzen, weisen fast gleich hohe katalytische Wirksamkeit auf.

(b) Dagegen zeigen die beiden Arten der Kupferoxyde, von denen das eine das aus Kupfersulfat und Natronlauge auf nassem Wege hergestellte pulverförmige und das andere zuerst mit verdünter Natronlauge getränkte und dann getrocknete drahtförmige Kupfoxyd war, beide gleich abnorm hohe katalytische Wirksamkeit.

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(1) I. Mitteil.: dies Bulletin, **13** (1938), 357; II. Mitteil.: *ebenda*, **13** (1938), 601; III. Mitteil.: *ebenda*, **13** (1938), 656; IV. Mitteil.: *ebenda*, **14** (1939), 9; V. Mitteil.: *ebenda*, **14** (1939), 520 und **15** (1940), 1; VI. Mitteil.: *ebenda*, **15** (1940), 47, 71; VII. Mitteil.: *ebenda*, **15** (1940), 119; VIII. Mitteil.: *ebenda*, **15** (1940), 166.

(c) Der ebenfalls mit Natronlauge getränkte und dann getrocknete Bimsstein ist auch für die in Rede kommende Austauschreaktion katalytisch wirksam, obwohl der Bimsstein an sich allein keine katalytische Wirksamkeit besitzt. Die Wirksamkeit des so mit Natronlauge behandelten Bimssteins ist aber viel kleiner als die des oben in (b) beschriebenen Natriumhydroxyd-tragenden Kupferoxyds.

Aus diesem Versuchsergebnisse kommt man zu dem Schluss:

(a) Die katalytische Wirksamkeit des Kupferoxyds wird weder durch die Herstellungsmethode noch durch die äusserliche Beschaffenheit viel beeinflusst, so lange als es chemisch rein bleibt.

(b) Die anormal hohe Wirksamkeit des auf nassem Wege unter Benutzung von Natronlauge hergestellten Kupferoxyds lässt sich vielleicht durch die Wirkung des in minimaler Menge zurückgebliebenen Natriumhydroxyds bzw. -oxyds erklären.

(c) Da die katalytische Wirksamkeit des mit Natronlauge behandelten Kupferoxyds nicht nur die des reinen Kupferoxyds sondern auch die des Natriumhydroxyd-tragenden Bimssteins übertrifft, hat man beim ersteren Fall mit der mischkatalytischen Wirkung von Kupferoxyd und Natriumhydroxyd zu rechnen.

Einleitung. Wir haben bisher die katalytische Wirkung verschiedener Arten der Oxyde und Metalle auf die Austauschreaktion der O-Atome zwischen gasförmigem Sauerstoff und Wasserdampf untersucht.

In der Praxis führten wir die Versuche im allgemeinen so aus, dass man unter Benutzung des bei verschiedenen Temperaturen direkt gemessenen prozentualen Austauschmasses $\%A$ solch eine Temperatur $t(10\%)$ interpoliert, wo das prozentuale Austauschmass $\%A$ an der Oberfläche des angegebenen Katalysators erst 10% erreicht, und die so bestimmte charakteristische Temperatur $t(10\%)$ der verschiedenen chemischen Arten der Katalysatoren untereinander vergleicht.

Während dieser Reihe der Versuche fanden wir oft, dass die Arten der Katalysatoren, die miteinander chemisch identisch sind aber auf voneinander verschiedene Weise hergestellt wurden, in einigen Fällen fast die gleiche dagegen in anderen Fällen wieder ziemlich beträchtlich abweichende katalytische Wirksamkeit manifestieren. So z.B. geben zwei Arten der Chromoxyde, Cr_2O_3-I und Cr_2O_3-II, die nach voneinander verschiedener Methode dargestellt wurden,[2] fast die gleiche hohe charakteristische Temperatur $t(10\%)$ an: $t(10\%)$ von Cr_2O_3-I beträgt 380°, während die von Cr_2O_3-II bei 420° liegt. Dagegen zeigen die ebenfalls auf zwei verschiedene Wege bereiteten Arten der Zinnoxyde, SnO_2-I und SnO_2-II,[3] zueinander ganz abweichende katalytische Wirksamkeit: $t(10\%)$ von SnO_2-I beträgt 400°, während die von SnO_2-II bei 670° liegt. Als eine plausible Ursache für diesen grossen Unterschied der katalytischen Wirksamkeit zwischen den beiden Arten der Zinnoxyde haben wir damals die Promotor- bzw. mischkatalytische Wirkung der Verunreinigungen angenommen, die bei der Herstellung der ersten Art Zinnoxyd SnO_2-I unbewusst und in minimaler Menge eingetreten sind.

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(2) Cr_2O_3-I wird durch die thermische Entwässerung des aus wässeriger Lösung von $Cr(NO_3)_3$ durch Versetzung mit verdünnter Ammoniaklösung abgeschiedenen Niederschlags von $Cr(OH)_3$ erhalten. Dagegen wird Cr_2O_3 II durch die thermische Zersetzung von $(NH_4)_2CrO_4$ hergestellt (Näheres darüber vgl. dies Bulletin, **14** (1939), 10 und **15** (1940), 53).

(3) SnO_2-I wird aus dem käuflichen Zinnoxyd bloss durch die starke Erhitzung bereitet, während SnO_2-II durch die thermische Zersetzung des Carbonats, das aus $SnCl_4$ unter Benutzung von Natronlauge und Kohlensäure hergestellt wurde, gewonnen wird (Näheres darüber vgl. dies Bulletin, **15** (1940), 51).

Dabei kommt als solch eine Verunreinigung, die die katalytische Wirksamkeit des angegebenen Zinnoxyds SnO_2-I anormal erhöhte, vor allem das Alkalihydroxyd in Frage, das bei der Herstellung des Oxyds verwendet aber daraus nicht vollständig befreit worden war. Diese Annahme liegt um so näher, als das betreffende Oxyd SnO_2-I nichts anders als das käufliche Oxyd war, das direkt vor dem Versuch durch blosse Erhitzung möglichst vollständig getrocknet wurde, während das andere weniger wirksame Oxyd SnO_2-II das unter besonderer Sorgfalt im eigenen Laboratorium synthetisch hergestellte Präparat war. Um diese Annahme sofort zu bestätigen haben wir deshalb in der vorliegenden Arbeit verschiedene Arten der Kupferoxyde auf verschiedene Wege hergestellt und ihre katalytische Wirksamkeit für die Austauschreaktion zwischen gasförmigem Sauerstoff und Wasserdampf miteinander sowie mit dem mit einer kleinen Menge Ätznatron absichtlich versetzten Kupferoxyd verglichen. Da wir aber bei diesem Versuch, wie erwartet, die stark erhöhte Wirksamkeit der mit Natriumhydroxyd möglicherweise bzw. absichtlich verunreinigten Kupferoxyde gefunden haben, wird weiter der mit Natronlauge getränkte Bimsstein betreffend seiner katalytischen Wirksamkeit für die in Rede kommende Austauschreaktion untersucht.

Darstellung der Katalysatoren. Die in der vorliegenden Arbeit verwendeten Arten der Katalysatoren werden auf folgende Weise hergestellt:

Kupferoxyd-I, CuO-I.—Als dieses wird das „Kupferoxyd drahtförmig" von Merck direkt zum Versuch verwendet.

Kupferoxyd-II, CuO-II.—Pulverförmiges reines Kupferoxyd aus dem Handel wird direkt zum Versuch benutzt.

Kupferoxyd-III, CuO-III.—Reines Kupfernitrat aus dem Handel wird in einem Porzellantiegel sorgfältig erhitzt bis keine Entwicklung von Stickstoffdioxyd mehr nachgewiesen wird. Das so erhaltene Kupferoxyd wird weiter in einem Quarzrohr unter Evakuierung bei etwa 500° einige Stunden lang erhitzt.

Kupferoxyd-IV, CuO-IV.—Reines basisches Kupfercarbonat aus dem Handel wird in einem Becherglas so lange erhitzt bis sich keine Kohlensäure mehr entwickelt. Dann wird das Oxyd in einem Quarzrohr ebenfalls wie beim CuO-III in Vakuum and bei 500° einige Stunden lang erhitzt.

Kupferoxyd-V, CuO-V.—Dieses Oxyd wird aus Kupfersulfat und Natronlauge dadurch bereitet, dass man den Niederschlag von Kupferoxyhydrat, der bei der Versetzung der wässrigen Lösung von reinem Kupfersulfat mit Natronlauge abgeschieden wird, durch Erhitzung entwässert. Den Niederschlag wäscht man nämlich zuerst gründlich mit destilliertem Wasser so lange, bis keine Sulfationen im Filtrat mehr nachgewiesen werden können. Dann wird der so gewaschene Niederschlag, nachdem er im Trockenschrank zuerst bei 80° aber zum Schluss bei 120° sorgfältig getrocknet worden ist, in einem Quarzrohr und zwar unter Evakuierung bei etwa 500° einige Stunden lang erhitzt, bis das Oxydhydrat sich vollkommen in Oxyd verwandelt.

Mischkatalysator aus Kupferoxyd und Ätznatron, CuO-NaOH.—Etwa 20 g „Kupferoxyd drahtförmig" von Merck, d.h. dasselbe Präparat wie

CuO-I, wird, nachdem es bei etwa 400° gut getrocknet worden ist, in 200 ccm 0.1 normaler Natronlauge eingeführt und darin etwa eine Stunde lange unter Vermeidung des Abdampfens des Wassers gekocht. Dann wird das Oxyd von der Lösung abfiltriert und ohne weiteres bei 400°C getrocknet. Das so behandelte Kupferoxyd dürfte höchstens 0.2% NaOH enthalten.

Ätznatron tragender Bimsstein, Bimsstein-NaOH.— „Bimsstein gekörnt" von Kahlbaum wird zunächst mit konzentrierter Salzsäure dreimal behandelt und dann mit destilliertem Wasser gründlich gewaschen, bis keine Chlorionen mehr im Filtrat sich nachweisen lassen. Der so gereinigte Bimsstein wird nun, nachdem er sorgfältig getrocknet worden ist, mit der 0.1 N Natronlauge auf genau dieselbe Weise wie oben bei der Herstellung des Kupferoxyd-Ätznatron-Mischkatalysators behandelt.

Versuchsergebnisse. Die Ergebnisse der Austauschversuche, die unter Verwendung der so hergestellten Arten Katalysatoren durchgeführt wurden, sind in Tabellen 1 bis 7 zusammengestellt, wo die Versuchsnr. in der ersten Spalte die zeitliche Reihenfolge der einzelnen Austauschversuche angibt und die sonstigen Buchstaben und Abkürzungen folgende Bedeutung haben:

Δs_a und Δs_e: der gewöhnlichem Wasser gegenüber gemessene Dichteüberschuss des zum Versuch verwendeten an schwerem Sauerstoff angereicherten schweren Wassers vor (Δs_a) und nach (Δs_e) dem Versuch.

$\Delta s_a(O)$: solch ein Anteil des gesamten anfänglichen Dichteüberschusses des schweren Wassers, der lediglich auf die Anreicherung der schweren Sauerstoffisotope zurückgeführt werden kann.

$\%A$: das „prozentuale Austauschmass", d.h. das prozentuale Verhältnis der wirklich gefundenen Dichteabnahme ($\Delta s_a - \Delta s_e$) des schweren Wassers nach der Austauschreaktion gegen den theoretischen Wert, der sich beim vollständigen Austausch ergeben würde.

M: Gewichtsmenge des zum Versuch verwendeten Katalysators.

Das zu jedem Versuch benutzte Reaktionsgasgemisch besitzt, wie üblich, die Zusammensetzung von $O_2:H_2O = 2:1$ und das im Katalysatorrohr beschickte Kupferoxyd wird bei jedem einzelnen Versuch direkt vor dem Beginn des Versuches immer bis auf etwa 800° unter Durchleitung des elektrolytischen Sauerstoffgases einige Stunden lang erhitzt.

Tabelle 1. CuO-I. $\Delta s_a = 54.2\,\gamma$, $\Delta s_a(O) = 34.5\,\gamma$, $M = 15$ g.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass $\%A$
2	500	53.6	0.6	2
4	600	50.3	3.9	14
1	700	36.5	17.7	61
3	800	25.6	28.6	99

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 2. CuO-II. $\Delta s_a = 54.2\,\gamma$, $\Delta s_a(O) = 34.5\,\gamma$, $M = 9$ g.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass $\%A$
2	500	53.2	1.0	3
4	600	48 9	5.3	18
1	700	26.5	27.7	96
3	800	25.9	28.3	98

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 3. CuO-III. $\Delta s_a = 54.2\,\gamma$, $\Delta s_a(O) = 34.5\,\gamma$, $M = 15$ g.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass $\%A$
5	400	54.2	0.0	0
2	500	54.3	- 0.1	0
4	600	51.3	2.9	10
1	700	27.8	26.4	91
3	800	25.0	29.2	101

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 4. CuO-IV. $\Delta s_a = 54.2\,\gamma$, $\Delta s_a(O) = 35.4\,\gamma$, $M = 6.5$ g.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass $\%A$
5	400	53.6	0.6	2
2	500	53.4	0.8	3
4	600	43.0	11.2	39
1	700	25.0	29.2	101
3	800	24.8	29.4	102

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 5. CuO-V. $\Delta s_a = 54.2\,\gamma$, $\Delta s_a(O) = 34.5\,\gamma$, $M = 10$ g.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass $\%A$
7	400	52.8	1.4	5
2	500	38.9	15.3	53
5	500	40.7	13.5	47
4	600	28.6	25.6	89
6	600	27.3	26.9	93
1	700	25.0	29.2	101
3	800	24.3	29.9	103

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 6. CuO-NaOH. $\Delta s_a = 54.2\,\gamma$, $\Delta s_a(O) = 34.5\,\gamma$, $M = 15$ g.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass $\%A$
5	300	53.0	1.2	4
2	400	50.9	3.3	11
4	500	52.1	2.1	7[4]
1	600	27.9	26.3	91
3	700	23.9	30.3	105

$$\%A = \frac{\Delta s_a - \Delta s_e}{28.9} \times 100$$

Tabelle 7. Bimsstein-NaOH. $\Delta s_a = 57.0\,\gamma$, $\Delta s_a(O) = 36.3\,\gamma$, $M = 6$ g.

Versuchsnr.	Temperatur °C	Δs_e in γ	$\Delta s_a - \Delta s_e$ in γ	Austauschmass $\%A$
2	500	55.4	1.6	5
1	600	51.8	5.2	17
3	700	51.3	5.7	19

$$\%A = \frac{\Delta s_a - \Delta s_e}{30.3} \times 100$$

Diskussion der Ergebnisse. Aus den oben angegebenen Versuchsergebnissen 1 bis 7 werden die von 1 bis 5, die unter Verwendung der fünf Arten der präparatisch reinen Kupferoxyde ausgeführt wurden, in untenstehender Abb. 1 graphisch wiedergegeben. Dabei werden auch die Versuchsergebnisse, die bei einem früheren Versuch unter Benutzung zweier Arten von Kupferoxyden gewonnen[5] und in III. Mitteil. berichtet wurden, zum Vergleich durch punktierte Linien eingezeichnet. Aus dieser graphischen Darstellung lässt sich aber ohne weiteres ersehen, dass die $\%A$-Temperatur-Kurven aller untersuchten Arten der Oxyde, ausgenommen die des letzten Oxyds CuO-V, sehr nahe zueinander liegen: die charakteristische Temperatur $t(10\%)$ der in der vorliegenden Arbeit untersuchten Arten der Oxyde, CuO-I bis CuO-IV, liegen etwa zwischen 550° und 600° und die der früher untersuchten beiden Arten der Oxyde liegen auch nicht viel weiter von diesem Temperaturgebiet. Der eventuell erkennbare kleine Unterschied der katalytischen Wirksamkeit zwischen

(4) Dieses abnorm kleine $\%A$ von Versuchsnr. 4 kann vielleicht dadurch erklärt werden, dass ein Teil des an der Oberfläche des Kupferoxyds anhaftenden Natriumhydroxyds aus irgend einem Grund verloren geht.

(5) Das eine Kupferoxyd, das damals CuO-I genannt wurde, ist nichts anders als das „Kupferoxyd drahtförmig" von Merck, das aber vor der Benutzung im Sauerstoffstrom bis auf 700° bis 800° über Nacht erhitzt wurde. Das andere Oxyd, das damals CuO-II genannt wurde, wird dagegen aus demselben käuflichen Präparat wie CuO-I dadurch bereitet, dass man dies, nachdem es zunächst mittels Wasserstoffgases vollständig bis zu Kupfer reduziert worden ist, wieder durch Erhitzung im Sauerstoffstrom bis zum Oxyd verwandelt (Näheres darüber vgl. dies Bulletin, **13** (1938), 658).

den betreffenden Arten der Oxyde[6] kann auf die verschiedene Oberflächenbeschaffenheit bzw. Oberflächengrösse zurückgeführt werden,[7] weil das in dem vorliegenden Versuch benutzte CuO-I drahtförmig, CuO-III feinkörnig, CuO-II und CuO-IV beide pulverförmig waren und die zu jedem Versuch benutzte Menge des Oxyds bei dem vorliegenden Versuch 7 bis 15 g während sie beim früheren Versuch (punktierte Linien I′ und II′ in Abb. 1!) etwa 65 g beträgt.

Gegen diese Übereinstimmung der katalytischen Wirksamkeit der ersten vier Arten der Oxyde, CuO-I bis CuO-IV, die in dem vorliegenden Versuch untersucht wurden, zeigt das zuletzt untersuchte Oxyd, CuO-V, das ebenfalls präparatisch als reines Kupferoxyd angesehen werden kann, viel höhere Wirksamkeit als die anderen Arten der Oxyde: die charakteristische Temperatur $t(10\%)$ dieses letzteren Oxyds CuO-V liegt sogar um 100° bis 150° niedriger als die anderen (vgl. Abb. 1). Diese grosse

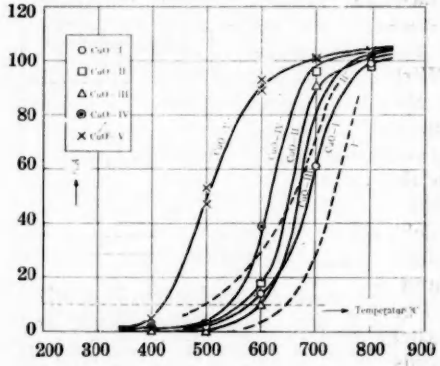

Abb. 1. Die Abhängigkeit des Austauschmasses von der Temperatur (CuO-I bis CuO-V).

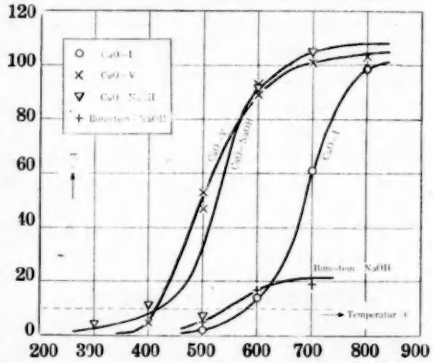

Abb. 2. Die Abhängigkeit des Austauschmasses von der Temperatur (CuO-I, CuO-V, CuO-NaOH und Bimsstein-NaOH).

Diskrepanz der katalytischen Wirksamkeit zwischen den präparatisch als gleich reines Kupferoxyd anzusehenden Katalysatoren, die uns an den ähnlichen Unterschied zwischen den früher untersuchten beiden Arten der Zinnoxyde erinnern lässt, legt uns die Annahme nahe, dass es sich dabei um die mischkatalytische Wirkung handelt, die von der bei der Herstellung des in Rede kommenden Oxyds CuO-V benutzten Natronlauge herrührt. Aus diesem Grunde wird in der nebenstehenden Abb. 2 die $\%A$-Temperatur-Kurve dieses letzteren Oxyds CuO-V mit der von CuO-

(6) Aus den $\%A$-Temperatur-Kurven in Abb. 1 ergibt sich, dass die charakteristische Temperatur t (10%) von CuO-III = 600°, die von CuO-I = 580°, die von CuO-II = 560° und die von CuO-IV = 550° ist; die katalytische Wirksamkeit der einzelnen Arten der Oxyde nimmt nämlich in dieser Reihe allmählich zu.

(7) Je grösser die Oberfläche des angebenen Katalysators wird, desto schneller muss die katalytische Austauschreaktion verlaufen. Dazu kommt aber noch die Möglichkeit, dass die störende Austauschreaktion zwischen schwerem Wasserdampf in der Gasphase und dem an der Oberfläche des Katalysators in minimaler Menge zurückhaftenden Sauerstoff bzw. Wasserdampf mit zunehmender Oberflächengrösse des Katalysators mehr in den Vordergrund tritt.

NaOH verglichen, das bei seiner Herstellung absichtlich mit einer kleiner Menge von NaOH versetzt worden ist. Die Abb. zeigt uns aber deutlich, dass die katalytische Austauschreaktion an der Oberfläche dieser beiden Arten der katalysatoren fast gleich leicht stattfindet: die characteristische Temperatur $t(10\%)$ beider Arten der Oxyde liegt sehr nahe nebeneinander. Aus diesem Ergebnisse wird deshalb zwanglos geschlossen, dass die enorm hohe Wirksamkeit von CuO-V wie erwartet vom Natriumhydroxyd herrührt, das bei der Herstellung des genannten Oxyds verwendet aber daraus nicht vollständig befreit worden war. Dabei können wir aber nicht ohne weiteres entscheiden, ob es sich um die direkte Wirkung des Natriumhydroxyds allein handelt oder ob irgendwelche von seinen Abarten, wie z.B. Natriumsalze d.h. Natriumionen eine Rolle spielen. Jedoch können wir in jedem Fall aus dem Versuchsergebnis, das unter Benutzung des mit Natriumhydroxyd getränkten Bimssteins gewonnen wurde, wohl schliessen, dass das Natriumhydroxyd auch in sehr verdünntem Zustand ziemlich starke katalytische Wirkung ausübt; die Kurve Bimsstein-NaOH in Abb. 2 zeigt, dass der Bimsstein, der an sich selbst fast keine katalytische Wirkung für die in Rede kommende Austauschreaktion besitzt (vgl. II. Mitteil.), fast ebenso gut wirksam wie das reine Kupferoxyd wird, wenn man den ersteren mit verdünnter Natronlauge behandelt.[8] Das oben angegebene CuO-NaOH wird ebenfalls mit Natronlauge von derselben Konzentration wie diese behandelt. Aber trotzdem ergibt die katalytische Wirksamkeit dieses Oxyds CuO-NaOH ebenso wie CuO-V, dass sie nicht nur die des reinen Kupferoxyds (d.h. von CuO-I bis CuO-IV) sondern auch die des NaOH-tragenden Bimssteins übertrifft. Dieser Befund legt uns deshalb die Annahme nahe, dass man durch die oben angegebene abnorm hohe Wirksamkeit des durch Natriumhydroxyd absichtlich (CuO-NaOH) bzw. unbewusst (CuO-V) verunreinigten Kupferoxyds mit einer mischkatalytischen Wirkung des Kupferoxyds und Natriumhydroxyds zu rechnen hat.

Den merklichen Unterschied der katalytischen Wirksamkeit, der oft zwischen den Arten der Katalysatoren gefunden wurde, die chemisch miteinander identisch sind aber auf verschiedene Weise hergestellt wurden, wie z.B. SnO_2-I und SnO_2-II, haben wir uns auch höchstwahrscheinlich aus demselben Grund wie oben, d.h. durch die mischkatalytischen Wirkung der unbewusst eingetretenen minimalen Mengen Verunreinigungen zu erklären. Aber anderseits können wir aus den Versuchsergebnissen mit den ersten vier Arten der Kupferoxyde CuO-I bis CuO-IV zwanglos zu dem Schluss kommen, dass der chemisch identische Katalysator ohne Unterschied seiner Herstellungsmethode und äusserlichen Beschaffenheit immer fast gleich hohe katalytische Wirksamkeit zeigt, so lange als er nicht nur als chemisch sondern auch katalytisch rein angesehen werden kann. Die früher gefundene Gleichheit der katalytischen Wirksamkeit der beiden Arten der Chromoxyde Cr_2O_3-I und Cr_2O_3-II, die auf verschiedene Weisen hergestellt wurden, gehört auch zu diesem letzteren Fall.

(8) Der verhältnismässig niedrige Wert von $\%A$, das mit Bimsstein-NaOH bei 700° gefunden wurde (vgl. Tabelle 7 Versuchsnr. 3), kann eventuell aus demselben Grund wie beim Versuch Nr. 4 mit CuO-NaOH bei 500° (in Tabelle 6), d.h. durch das Verlorengehen eines Teils von NaOH erklärt werden (vgl. Fussnote (4)).

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The Occurrence of Gallium in the Hot Springs of Japan.

By **Kazuo KURODA.**

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Gallium is widely distributed in nature in minute quantities, and it is detected spectroscopically in many rocks and minerals. It is, however, rarely reported in the mineral waters. J. Bardet[1] found this element in some French mineral waters, and S. Piña de Rubies and C. Sirvent d'Argent[2] in Spanish mineral waters. According to V. M. Goldschmidt,[3] the atomic ratio of gallium to aluminium in the aluminium minerals varies from 1:10 to 1:100000. The present author found the occurrence of gallium in a number of hot springs, mainly of acid alum-vitriol springs of Japan. Their gallium content was spectroscopically estimated.

Arc Spectrographic Estimation of Gallium. Pure gallium metal was dissolved in hydrochloric acid and the solutions containing 1, 0.1, 0.01, 0.001 and 0.0001 mg. of gallium per c.c. were prepared. Sodium chloride (10 mg.) was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001 and 0.0001 mg. of gallium respectively. The Hilger spectrograph of E2 type was used. The spectral lines observed at different concentrations are described in Table 1. In this table, S signifies that the line in question is strong, W that it is weak and F that it is faintly visible.

(1) J. Bardet, *Compt. rend.* **157** (1913), 224.
(2) S. Piña de Rubies, C. Sirvent d'Argent, *Anal s soc. españ. fis. quím.* **29** (1931), 235; *Chem. Abstracts*, **25** (1931), 3104.
(3) V. M. Goldschmidt, Cl. Peters, *Nachr. Ges. Göttingen, Math.-physik. Klasse* **1931**, 165-85 (1931).

Table 1. Spectral Lines at Different Concentrations.

λ (Å)	1 mg.	0.1 mg.	0.01 mg.	0.001 mg.	0.0001 mg.
2255.03	F				
2259.23	F				
2294.20	W	F			
2297.87	W	F			
2338.60	S	W			
2371.33	S	W			
2418.70	S	W	F		
2450.08	S	S	W		
2500.71	S	S	W	F	
2659.87	S	S	W	F	
2719.66	S	S	W	F	
2874.24	S	S	S	S	F
2943.7	S	S	S	S	W
2944.18	S	S	W	F	
4033.01	S	S	S	F	
4172.06	S	S	W	F	

Gallium Content of the Hot Springs of Japan. Aluminium oxide (10 mg.) obtained from the suitable quantities (5 to 50 c.c.) of the mineral water was subjected to arc excitation. The following gallium lines were found (Table 2). Table 2 shows that seven samples (out of eleven samples) contained about 0.1 γ of gallium in 10 mg. of aluminium oxide. The gallium content of the hot springs was calculated from their aluminium content. The results are shown in Table 2 and Table 3.

Except the hot springs of Yunohanazawa, gallium was always found in the above-mentioned acid alum-vitriol springs of Japan. The atomic

Table 2. Spectral Lines of Gallium.

Hot Spring	Prefecture	2874.24 Å	2943.7 Å
(1) Kinbu.	Yamanasi	—	W
(2) Seki-no-Yu, Kusatu.	Gumma	W	S
(3) Sirahata-no-Yu, Kusatu.	Gumma	F (?)	W
(4) Zizo-no-Yu, Kusatu.	Gumma	—	W
(5) Wasi-no-Yu, Kusatu.	Gumma	—	W
(6) Takayu.	Yamagata	—	F
(7) Kinkei.	Totigi	—	—
(8) Gongen-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—
(9) Kōbō-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—
(10) Yoemon-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—
(11) Daruma-Zigoku, Yunohanazawa, Hakone.	Kanagawa	—	—

Table 3. Gallium Content of the Hot springs of Japan.

Hot Spring	Gallium Contents (g./l.)
(1) Kinbu.	$1\sim 5\times10^{-5}$
(2) Seki-no-Yu, Kusatu.	$5\sim10\times10^{-6}$
(3) Sirahata-no-Yu, Kusatu.	$1\sim 5\times10^{-6}$
(4) Zizo-no-Yu, Kusatu.	$1\sim 5\times10^{-6}$
(5) Wasi-no-Yu, Kusatu.	$1\sim 5\times10^{-6}$
(6) Takayu.	$1\sim 5\times10^{-6}$
(7) Kinkei.	$5\sim10\times10^{-7}$
(8) Gongen-Yu, Yunohanazawa.	less than 10^{-7}
(9) Kōbō-Yu, Yunohanazawa.	less than 10^{-7}
(10) Yoemon-Yu, Yunohanazawa.	less than 10^{-7}
(11) Daruma-Zigoku, Yunohanazawa.	less than 10^{-7}

ratio of gallium to aluminium in the hot springs is considered to be 1:100000. Expressed in percentages to total residue, the gallium content of these hot springs is between 0.001 and 0.00001.

Summary.

(1) An arc spectrographic detection and estimation of gallium was studied.

(2) The gallium content of a number of hot springs of Japan was estimated.

The author expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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The Occurrence of Beryllium in the Hot Springs of Japan.

By Kazuo KURODA.

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In the previous paper,[1] the author reported the beryllium content of the hot springs of Matunoyama in Niigata Prefecture. Beryllium has recently been detected spectroscopically in a number of hot springs,

Table 1. Spectral lines of Beryllium.

Hot Spring	Prefecture	2348.6Å	2494.7Å	2650.8Å	3131.1Å
(1) Kinbu.	Yamanasi	W	—	F	F
(2) Seki-no-Yu, Kusatu.	Gumma	W	—	—	—
(3) Sirahata-no-Yu, Kusatu	Gumma	W	—	—	F
(4) Zizo-no-Yu, Kusatu.	Gumma	—	—	—	—
(5) Wasi-no-Yu, Kusatu.	Gumma	F	—	—	—
(6) Takayu.	Yamagata	—	—	—	—
(7) Kinkei.	Totigi	F	—	—	—
(8) Gongen-Yu, Yunohanazawa, Hakone.	Kanagawa	—	—	—	—
(9) Kōbō-Yu, Yunohanazawa, Hakone.	Kanagawa	W	F (?)	F	F
(10) Yoemon-Yu, Yunohanazawa, Hakone.	Kanagawa	F	—	—	—
(11) Daruma-Zigoku, Yunohanazawa, Hakone.	Kanagawa	W	F	F	F

Table 2. Beryllium Content of the Hot Springs of Japan.

Hot Spring	Beryllium Content (g./l)
(1) Kinbu.	$5 \sim 10 \times 10^{-5}$
(2) Seki-no-Yu, Kusatu.	1×10^{-6}
(3) Sirahata-no-Yu, Kusatu.	$1 \sim 5 \times 10^{-6}$
(4) Zizo-no-Yu, Kusatu.	less than 10^{-7}
(5) Wasi-no-Yu, Kusatu.	$5 \sim 10 \times 10^{-7}$
(6) Takayu.	less than 10^{-7}
(7) Kinkei.	$5 \sim 10 \times 10^{-7}$
(8) Gongen-Yu, Yunohanazawa.	less than 10^{-7}
(9) Kōbō-Yu, Yunohanazawa.	$1 \sim 5 \times 10^{-6}$
(10) Yoemon-Yu, Yunohanazawa.	$5 \sim 10 \times 10^{-7}$
(11) Daruma-Zigoku, Yunohanazawa	$1 \sim 5 \times 10^{-6}$

(1) This Bulletin, **14** (1939), 305.

mainly of acid alum-vitriol springs of Japan. The amount of beryllium in these hot springs was spectroscopically estimated.

Aluminium oxide (10 mg.) obtained from the suitable quantities (5 to 50 c.c.) of the mineral water was subjected to arc excitation, and the following beryllium lines were found (Table 1.). The amount of beryllium was estimated from the table of the spectral lines of beryllium at different concentrations, which was described in the previous paper.[1] The results of the experiment are shown in Table 2.

The results of the experiment show that the atomic ratio of beryllium to aluminium in most of acid springs above-mentioned is considered to be 1:100000. Expressed in percentages to total residue, the beryllium content of these hot springs is between 0.001 and 0.00001.

Summary.

The beryllium content of a number of hot springs of Japan was estimated.

The author expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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